

SELENIUM SAMPLING AND ANALYSIS IN COAL COMBUSTION SYSTEMS

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BACKGROUND

The Clean Air Act Amendments of 1990 (CAAA) identified 189 elements and compounds that are classified by the U.S. EPA as hazardous air pollutants (HAPs). Among these are eleven inorganic trace elements found in coal. A provision of the CAAA required EPA to conduct a study of the health and environmental impacts of HAP emissions from electric utility generating units. EPA has completed a number of draft documents in compliance with this mandate. For trace element emission estimates, they have relied on a number of field tests which were conducted by a variety of organizations including the U.S. Department of Energy (DOE). The DOE program utilized the EPA Method 29 sampling train to measure the emissions of trace elements including Se. EPA Method 29 is validated for municipal waste combustor sampling but not for coal-fired combustion sources.

The DOE program involved measurements at eight coal-fired utilities selected to represent a cross-section of the coal-fired utility industry in regard to fuels and furnace configurations. Five sampling teams performed the testing. All of the test teams reported low material balance closures for Se.¹ CONSOL R&D participated at two of these test sites: Minnesota Power Clay Boswell and Illinois Power Baldwin stations. The Se balance closures for the Boswell plant ranged from 12% to 21% and averaged 18.5%.² The Se balance closures for the Baldwin plant ranged from 30% to 60% and averaged 50%.³ Selenium is the only element that showed a material balance closure problem for both test sites, indicating either a sampling or analytical error. At the third DOE Air Toxics Working Group Meeting, the poor Se balances obtained from the eight station tests were discussed, but there were no clear answers as to the cause. The fact that all of these programs showed low Se balance closures is evidence of a sampling or analytical problem.

After reviewing these results, CONSOL R&D conducted a sampling and analytical program to determine the reasons for the poor Se material balances. This program focused on two areas: 1) the accuracy of sampling and analytical procedures for measuring Se in solids, and 2) the potential for Se losses within the combustion or sampling system.

Selenium Properties

Among the eleven trace elements listed as HAPs, Se has unique volatility characteristics that could result in sampling problems. All of these eleven elements except mercury (Hg) and Se are predominantly (>99%) in the solid phase at coal-fired flue gas temperatures.^{4,5} For these non-volatile elements, flue gas sampling is not required to complete a material balance. Because of its vapor pressure, almost all of the Hg released during combustion should be present as a vapor.

The equilibrium vapor pressure curve (Figure 1) for Se (as SeO_2) indicates that this element can be present in both the gas and solid phases at normal utility flue gas temperatures.⁶ The curve shows that there can be a large change in the partitioning of SeO_2 between the gas and solid phases in the temperature range of 200 °F to 300 °F. This temperature range is important because it encompasses the typical flue gas exhaust temperature for utilities (~280 °F to 300 °F) and the operating temperature of the EPA Method 29 probe and filter (258 °F \pm 20 °F). The Se content in the Illinois coal fired at the Baldwin plant was 4 ppm (whole coal basis). If all the Se in the coal volatilized during combustion, this would result in a gas phase Se concentration of approximately 97 ppbv. As the flue gas cools, some fraction of the gas phase Se would condense. Table 1 shows the theoretical distribution of Se between the vapor and condensed phases at various temperatures.

Selenium is the only Clean Air Act trace element that undergoes this phase transition in this temperature window. The implication of this phenomenon on Se sampling results is discussed below.

Selenium in U.S. Coals

There is a limited amount of information on the Se contents of commercial (i.e., as-fired) coals. CONSOL has collected trace element data on over 250 coal samples representing a wide cross-section of U.S. coal production. This database shows a Se-in-coal concentration range of 0.5 to 6.5 ppm (whole-coal basis) with an average of ~1.5 ppm.⁷ The recent DOE program involved nine coals with Se concentrations between 0.85 ppm and 3.25 ppm. In a DOE-sponsored coal analysis

round robin study conducted by CONSOL R&D, Se determinations for a NIST reference coal ranged from 0.75 ppm to 1.52 ppm compared to a certified value of 1.29 ppm. Accuracies ranged from 42% low to 15% high. Only one of the ten reported values was within 10% of the certified value.⁸ The difficulty in obtaining an accurate Se-in-coal determination at concentrations typical for coal is certainly a contributing factor to the uncertainty in material balance closures.

Emission Factors

Trace element emission factors for combustion sources are developed by using the trace element concentration in the fuel and calculating a maximum uncontrolled emission rate. This value then is adjusted to account for bottom ash-to-fly ash partitioning, particulate-to-gas partitioning, and removal in control devices. In many cases these partitioning factors are estimated from the best available test data. If possible, the estimated emission factor is compared with emission measurements. The phase distribution of Se makes estimation of partitioning and removal factors difficult and uncertain.

The difficulty in closing Se balances around coal-fired power plants leads to uncertainty in the validity of the measured emissions and estimated emission factors based on these measurements. The accuracy of emission estimates is important because they ultimately will be used in risk assessments.

RESULTS AND DISCUSSION

This research program was focused on two areas of concern:

- Analysis of selenium in process stream samples,
- Se losses in the flue gas ducts and EPA Method 29 sampling train.

Analysis of Selenium in Process Stream Samples

There are three factors that contribute to good material balance closures: obtaining a representative sample, accurately measuring the process stream flow-rate, and an accurate chemical analysis. Assuming that the first two conditions are met, the chemical analysis becomes the most important step. However, the determination of selenium in process stream samples can be difficult.

Table 2 shows the results of Se analyses conducted on a NIST coal ash standard. These data show that the digestion step outlined in Method 29 procedures may not be suitable for all solid materials.⁴ The Method 29 digestion (SW 846) involves the digestion of ~0.5 g of solids with 6 mL of concentrated HNO₃ and 4 mL of concentrated HF and either conventional heating in a Parr Bomb at 285 °F (six hours) or microwave heating. This digestion showed a low recovery for Se and for all of the HAPs elements. The CEM microwave procedure involves a multi-stage digestion using the same acids outlined in the Method 29 technique, but with larger volumes and longer digestion times. This technique showed a very good Se recovery. The open-vessel technique showed low recoveries for Se, although previous analyses of this ash standard have shown excellent recoveries for Se and the non-volatile trace elements. The low Se recoveries specific to this determination are thought to be a result of uncontrolled fluctuations in the temperature used in the digestion. Because of the low results for Se by open vessel digestion, CONSOL R&D analyzed a variety of solids for Se by first preparing the sample using hydropyrolysis. In this procedure, the solids are pyrolyzed in a stream of excess air and steam. The volatile Se is passed through a condenser and then into a NaOH scrubber solution for Se capture. This solution is analyzed by ICP-MS. The efficiency of this procedure has been verified by the analysis of SARM, NIST, and NBS standards.

The open-vessel digestion technique has several advantages. It is safer than the microwave technique, more time-efficient than the other procedures, and provides excellent elemental recoveries for most of the trace elements of interest (Hg determinations are obtained using a separate sample preparation technique). This work indicates that Se may be lost during the open vessel digestion step and additional work is being completed to determine the critical digestion temperature for this procedure for a variety of coal ash matrices.

Conclusions drawn from these data are that the Method 29 procedure does not provide a sufficiently rigorous digestion for coal ash samples. Typical coal fly ash has a strong clay-silicate matrix which requires either a more rigorous digestion or larger quantities of the acids. The same criticism applies to the analysis of the Method 29 solid fraction. These data indicate the front-half filter analysis can be biased low, which would lead to inaccurate material balance closures.

Selenium Losses in the Flue Gas Ducts and Sampling Train

Because the Se analyses of the coal, ash, and Method 29 front-half samples could be in error, Se material balances from the sampling programs at the Baldwin² and Boswell³ plants were recalculated based on analyses obtained using the hydropyrolysis digestion techniques for the process stream (coal and ash) samples. The Method 29 samples were not available for repeat analyses. The ash samples showed somewhat higher Se concentrations, but the increase had only a small

effect on the Se balances. The selenium balances for the Baldwin testing are shown in Table 3.

These data indicate the Se material balance closures are low by -50%. The Se input value is based on the Se in the coal which averaged 3.73 ppm (whole-coal basis) for these tests. This analysis was verified as part of the DOE round robin which involved a comparative analysis by five labs. The Se values in the ESP ash samples were verified through replicate analyses and comparison with standard reference materials. The temperature of the flue gas entering the ESP was -340 °F and -330 °F at the sampling location. The vapor pressure curve for Se₂ at these temperatures indicates that all of the available Se should have been present in the vapor state. This is supported by the low level of Se in the ESP ash samples. The Method 29 procedure calls for a front-half (probe and filter) temperature of 258 °F ±20 °F. The vapor pressure curve at 250 °F predicts a gas phase Se concentration of 8 ppbv. This value is very close to the observed values (4, 6, and 7 ppbv).

A possible explanation for the poor Se balance for this utility is that at the Method 29 front-half sampling temperature (258 °F ±20 °F), the equilibrium between gas phase and solid phase Se is shifted to the solid phase. In reviewing the field sampling sheets, it was noted that the normal variations in the heater box gave temperatures as low as 240 °F. As shown in Figure 1, the selenium vapor pressure at 240 °F corresponds to a gas phase Se concentration of only 3.5 ppbv, which is well below what would be expected at the flue gas temperature. The speculation becomes more severe at lower temperatures and could be aggravated by insufficient heat to the sampling probe. If condensation occurs, the measurement of the Se emissions becomes a function of the accuracy of the front-half (solid) fraction. For this program, the front-half analyses were found to be unreliable,^{2,3} and it was assumed that the particulate phase Se was represented by the ESP hopper ash samples. However, the ESP solids were collected at a point in the gas stream where the gas temperature is -340 °F. At this temperature, almost all of the Se is in the gas phase. It is likely that a significant fraction of the gas-phase Se condensed in the front-half of the Method 29 sampling train and was unaccounted for due to the inability to obtain an accurate front-half (particulate) Se analysis.

CONSOL Pilot-Scale Selenium Sampling Results

CONSOL R&D conducted a series of 12 Se measurements on the flue gas from a 1.5 MM Btu/hr pilot-scale coal combustor (Figure 2). All measurements were taken under tightly controlled combustion conditions using a constant coal source. The only variable was the flue gas temperature. The gas phase emission results from this test and the associated gas and sampling temperatures were compared. The test with the lowest flue gas temperature (200 °F) also showed the lowest concentration of gas phase Se (2.9 ppbv). The test with the highest flue gas temperature (335 °F) resulted in the highest gas phase Se concentration (9.3 ppbv).

The percent of the available Se found in the gas phase ranged from 11% to 34% and this value was dependent on the temperature of the flue gas and sampling equipment. Vapor pressure has an exponential dependence on temperature. However, because the temperatures are within a narrow range, a linear correlation analysis was conducted on the data to assess the co-variance of gas phase Se concentrations with flue gas and sampling temperatures. The following correlations were obtained from this data set:

Gas Phase Se Concentration Correlated to:	r ²
Duct Temperature	0.77
Probe Temperature	0.51
Filter Temperature	0.23

These data show that the gas phase Se is moderately well correlated with the temperature of the flue gas and (more weakly) with the temperature at which the solids are collected in the Method 29 train. These data suggest that the partitioning between gas and solid phase is influenced by these temperatures and supports the mechanisms previously discussed. The data also show that cold spots in the flue gas handling system or the sampling probe can decrease the apparent gas phase Se concentration (Figure 2). A decrease in temperature between one sampling position to the next, in the temperature window of 200 °F to 300 °F could deplete the vapor phase Se by deposition on the sidewalls or on fly ash solids.

CONCLUSIONS

- * The Method 29 analytical procedure (including SW 846 digestion) shows a low bias for most trace elements commonly found in coal ash, including Se.

- * Analytical bias (due to Se volatilization) can occur during the sample preparation (digestion) stage.
- * Se partitioning is influenced by the gas and sampling temperatures.
- * The Method 29 Sampling procedure can shift the apparent speciation between gas phase and solid phase Se.
- * Material balance closures can be affected if vapor phase and solid phase samples are taken at different flue gas temperatures.
- * The simultaneous sampling and analysis of Se in conjunction with the other elements as described in EPA Method 29 may lead to an inaccurate Se determination.

RECOMMENDATIONS

This work represents an initial step to a more complete understanding of Se sampling in coal combustion systems. There are a number of research areas that should be further investigated to improve this understanding and improve emission measurements. Recommendations for future research are as follows:

- * Conduct comparative M-29 sampling with the front-half temperature at 258°F and at the actual duct temperature.
- * Analyze M-29 front-half Se concentrations by both the SW-846 technique and the hydropyrolysis method.
- * Investigate more effective digestion techniques for Se analysis of solid samples.
- * Conduct a Se balance program around a well-controlled system using the suggested modifications.

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Table 1. Theoretical Phase Distribution for Se Emissions

Temperature, °F	Solid Phase (Fly ash)		Vapor Phase	
	ppmw (a)	% of Total	ppbv	% of Total
220	130	98%	1.9	2%
240	127	96%	3.5	4%
260	117	87%	13	13%
280	90	67%	32	33%
300	33	24%	74	76%

- (a) Based on 10% ash in coal, 70% bottom ash - 30% overhead ash ratio, and no Se in bottom ash

Table 2. Comparison of Se Results on NIST 1633a

Element	Reference Value, ppm	SW-846 Digestion ^a	Microwave Digestion ^b	Open Vessel Digestion ^c
Arsenic	145	110	155	141
Beryllium	12*	2.1	11.2	12.7
Cobalt	46.0	7.7	109	42.6
Lead	72.4	12.7	50.9	74.0
Manganese	179	33.6	157	195
Nickel	127	17.3	113	117
Selenium	10.3	7.66	11.1	4.4
Vanadium	297	62.2	286	283

*Designates informational values

- a) Digestion and analytical procedure described in M-29⁹
 b) Digestion and analytical procedure developed by CEM Corporation⁹
 c) Digestion and analytical procedure developed by CONSOL R&D^{2,3}

Table 3. Selenium Mass Flowrates for the Baldwin Process Streams (unit is lb/hr*)

	Test 1	Test 2	Test 3
Coal Input	1.82 (122)	1.78 (120)	1.39 (94)
Bottom Ash	0.03	0.03	0.03
Econ. Ash	0.00	0.00	0.00
ESP Ash	0.02	0.02	0.01
Stack Solids**	0.96 (64)	0.42 (28)	0.60 (40)
Stack Vapor**	0.09 (6)	0.06 (4)	0.10 (7)
Se Closure	60%	30%	53%

- * The values inside the parentheses indicate the theoretical vapor phase concentration in ppbv if all of the Se present was volatilized
 ** Values obtained from the Method 29 sampling train

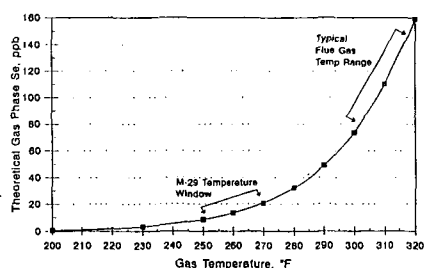
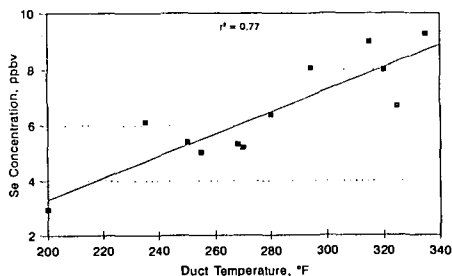
Figure 1. Vapor Pressure Curve for SeO_2 .

Figure 2. Gas Phase Se Concentrations vs Duct Temperature.